# Azonia-azulene Salts. Part I. Synthesis of Some 9-Hydroxypyrrolo-[1,2-*a*]azepinium Salts and 10-Hydroxyazepino[1,2-*a*]indolium Salts

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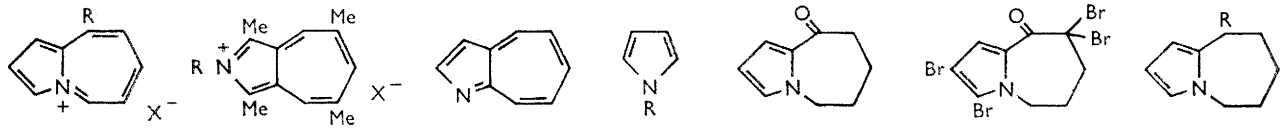
The syntheses of 1,2,3-tribromopyrrolo[1,2-*a*]azepin-9-one (23) and 11-methylazepino[1,2-*a*]indol-10-one (20), by a one-step elimination reaction from 1,2,3,8,8-pentabromo-6,7,8,9-tetrahydro-5*H*-pyrrolo[1,2-*a*]azepin-9-one (22) or 9,9-dibromo-7,8,9,10-tetrahydro-11-methyl-6*H*-azepino[1,2-*a*]indol-10-one (19) respectively, are described. The structures of the azepinones were established from their n.m.r. spectra and by hydrogenation of the pyrroloazepinone (23). Both azepinones on protonation gave hydroxyazonia-azulene salts; the pyrroloazepinone (23) with Meerwein's reagent gave 1,2,3-tribromo-9-ethoxypyrrolo[1,2-*a*]azepinium fluoroborate (25).



A detailed examination of the quinolizinium salts [1,2] has led us to an interest in the possibility of causing such aromatic but positively charged salts to undergo electrophilic substitution [3-7] as well as the more common nucleophilic substitution.[8,9] This in turn leads to a consideration of the anticipated properties of the azonia-azulene systems, notably those carrying a nitrogen atom at the bridgehead (1). The only example of an azonia-azulene salt in the literature was the compound (2) [10] although the aza-azulene (3) was reported.[11] In this paper we present a route to some substituted azonia-azulene salts of type (4); in subsequent papers we shall report theoretical calculations on the effect of a positive nitrogen at various points in the azulene ring, and properties of the salts (4) and the intermediate azepinones.



(1) R = H
(4) R = OH

(2)

(3)

(5) R = $[CH_2]_4Cl$
(6) R = $[CH_2]_4$·CN

(7)

(8)

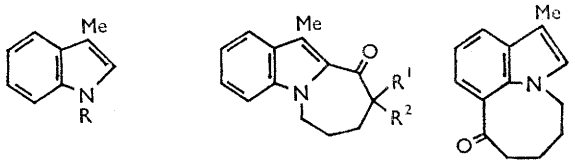
(9) R = OH
(10) R = OBz

Our first attempts were modelled on the well known approaches to benzotropones *via* bromination–dehydrobromination sequences.[12] The required bicyclic ketone was prepared by a modification of the procedure described by Patterson *et al.*; [13] from sodium pyrrolide and 4-tolylsulphonyloxybutyl chloride we obtained the chlorobutylpyrrole (5), improving the reported yield by an inverse addition technique. The chlorobutylpyrrole (5), with sodium cyanide in dimethyl sulphoxide, gave the cyanide (6) (54%); cyclisation with boron trifluoride and hydrolysis of the imine so formed gave the ketone (7), again in improved yield. We had hoped that the acyl substituent might deactivate the pyrrole ring sufficiently to allow bromination only α to the carbonyl function; however, a variety of brominating agents showed roughly equal rates of pyrrole bromination and bromination α to the ketonic carbonyl. The use of bromine in less than five-molar ratio gave mixtures from which a crystalline tetrabromo-ketone (two bromine atoms in the pyrrole ring), which is tentatively assigned structure (8), was obtained. A second approach to the introduction of unsaturation into the seven-membered ring involved the reduction of the ketone (7) with sodium borohydride to give the alcohol (9), which formed a benzoate (10). Slight warming (50°) caused the production of white crystals of benzoic acid, but the residue was black and, possibly, polymeric.

To simplify the bromination experiments we decided to work with a pyrrole with only one free nuclear position; the easiest derivative of this type to obtain was 3-methylindole (11). The 3-methylindolide ion reacted with 4-tolylsulphonyloxybutyl chloride to give the chlorobutylindole (12), converted by sodium cyanide in dimethyl sulphoxide into the nitrile (13). We were unable to cyclise the nitrile (13) to the tricyclic ketone (16) with boron trifluoride or with polyphosphoric acid; the latter reagent gave the amide (14), a product previously obtained in attempts to cyclize nitriles with polyphosphoric acid.[14] Hydrolysis of the nitrile gave a high yield of the acid (15), which was cyclised by polyphosphoric acid to the cyclic ketone (16). Although we would expect electrophilic attack to take place preferentially at the indole 2-position to give ketone (16), rather than at position 7 to give the isomer (17), we could confirm the structure of the cyclisation product by virtue of the disappearance of the indole 2-proton, clearly shown as a singlet near δ 6·9 p.p.m. in the n.m.r. spectra

[1] E. E. Glover and G. Jones, *J. Chem. Soc.*, 1958, 3021; A. R. Collicutt and G. Jones, *ibid.*, 1960, 4101.
[2] A. Fozard and G. Jones, *J. Chem. Soc.*, 1964, 2763.
[3] A. Fozard and G. Jones, *J. Chem. Soc.*, 1963, 2203.
[4] P. A. Duke, A. Fozard, and G. Jones, *J. Org. Chem.*, 1965, **30**, 526.
[5] A. Fozard and G. Jones, *J. Chem. Soc.*, 1964, 2760.
[6] A. Fozard and G. Jones, *J. Chem. Soc.*, 1964, 3030.
[7] T. L. Hough and G. Jones, *J. Chem. Soc.* (*C*), 1968, 1088.
[8] T. Miyadera, E. Ohki, and I. Iwai, *Chem. and Pharm. Bull.* (*Japan*), 1964, **12**, 1344.
[9] T. Miyadera, *Chem. and Pharm. Bull.* (*Japan*), 1965, **13**, 503.
[10] A. V. El'tsov, A. A. Ginesina, and L. N. Kivokurtseva, *Tetrahedron Letters*, 1968, 735.
[11] T. Nozoe, S. Seto, S. Matsumara, and T. Terasawa, *Chem. and Ind.*, 1954, 1357.
[12] For example, G. L. Buchanan, and D. R. Lockhart, *J. Chem. Soc.*, 1959, 3586.
[13] J. M. Patterson, J. Brasch, and P. Drenko, *J. Org. Chem.* 1962, **27**, 1652.
[14] E. Lathwood and H. Suschitzky, *J. Chem. Soc.*, 1964, 2477.

of compounds (11)—(15) but absent in that of the ketone (16).



(11) R = H
(12) R = $[CH_2]_4Cl$
(13) R = $[CH_2]_4$·CN
(14) R = $[CH_2]_4$·CO·$NH_2$
(15) R = $[CH_2]_4$·$CO_2H$

(16) $R^1 = R^2 = H$
(18) $R^1$ = H, $R^2$ = Br
(19) $R^1 = R^2$ = Br

(17)

We first experimented with bromination of the ketone (16) in an attempt to obtain the monobromo-derivative (18); even under mild conditions a mixture of mono- and dibromo-ketones was obtained. We obtained a high yield of the dibromo-ketone (19) by use of phenyltrimethylammonium tribromide.[15] The pale yellow dibromo-ketone showed a carbonyl stretching frequency of 1668 $cm.^{-1}$; treatment with lithium chloride in boiling dimethylformamide (selected as a relatively mild

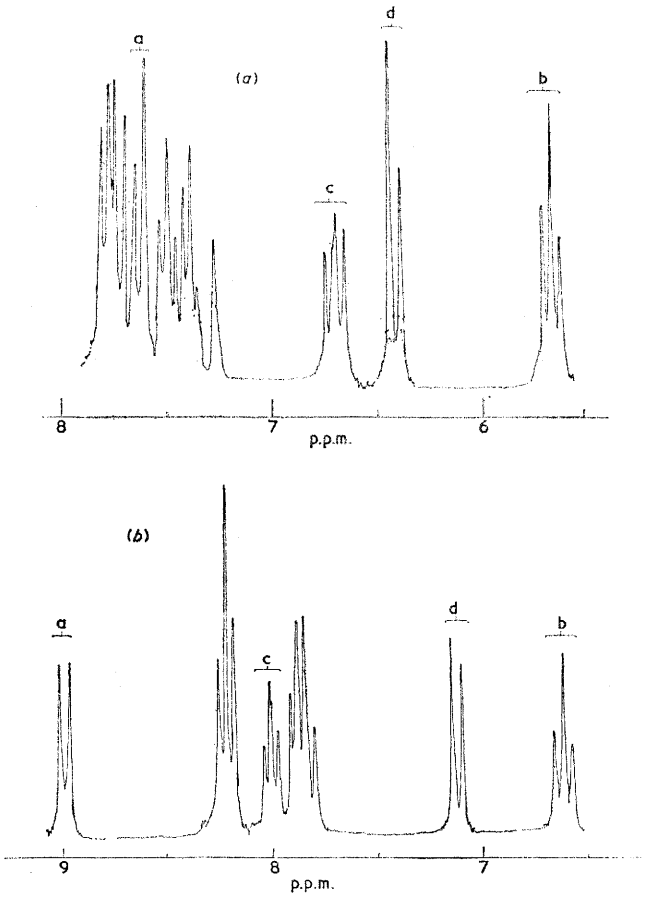
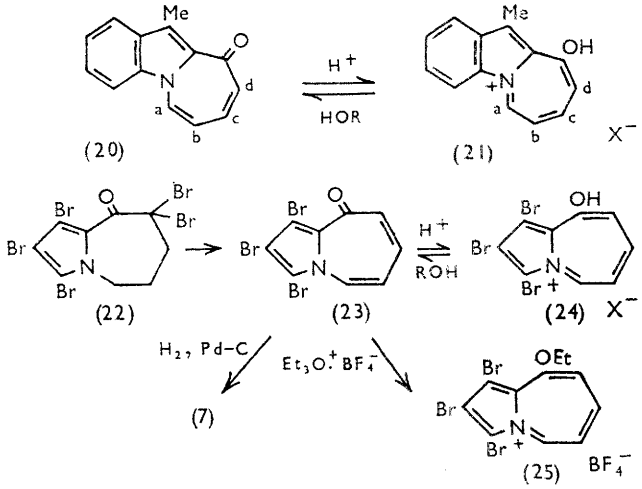



FIGURE 1 (*a*) Azepinoindolone (20), aromatic region, in $CDCl_3$; (*b*) azepinoindolium (21), aromatic region, in TFA

dehydrobrominating agent[16]) gave, in high yield, an orange compound with carbonyl stretching at 1656, 1603, and 1570 $cm.^{-1}$. Micro-analysis agreed with a formula $C_{14}H_{11}NO$ and indicated removal of two molecules of hydrogen bromide. Solutions of the dehydrobromination product in trifluoroacetic or other strong acids were deep blue; all these observations suggested structure (20) for the orange dehydrobromination product and this was confirmed by the n.m.r. spectra (220 MHz) (Figure 1). Protonation gave the azonia-azulene system (21) and satisfactory analyses were obtained for the bromide (21; X = Br); the n.m.r. spectrum of the protonated form (220 MHz) is also given in Figure 1. The salts (21) are very unstable to hydroxylic solvents and are immediately reconverted into the azepinoindolone (20) in alcoholic solution.

The simplicity of this route to the tricyclic azonia-azulene system led us to return to the bicyclic ketone (7). Bromination with bromine (5 mol.) gave the penta-bromo-ketone (22); again this was smoothly converted




in high yield by lithium chloride in dimethylformamide into the dehydrobrominated material. Analysis indicated the formula (23) which was again confirmed by the n.m.r. spectrum (Figure 2). Protonation gave the reddish-orange hydroxyazonia-azulene salts (24), of which the bromide (24; X = Br) gave satisfactory analyses. The n.m.r. spectrum of the protonated form is also shown in Figure 2. Reaction between the azepinone (23) and triethyloxonium fluoroborate gave the ethoxyazonia-azulenium salt (25). Finally, the azepinone (23) was reduced catalytically to the bicyclic ketone (7), with removal of the three bromine atoms, indicating that the pyrroloazepinone (23) retained the original 5 : 7 bicyclic skeleton, and that no ring contraction or expansion had taken place.

The 220 MHz spectra of compounds (20) in deuteriochloroform and in trifluoroacetic acid [as (21)] are shown in Figure 1; those of the bicyclic system (23) and (24) are given in Figure 2. An assignment can be made of all the protons on the seven-membered rings and coupling

[15] A. Marquet and J. Jacques, *Bull. Soc. chim. France*, 1962, 90.
[16] P. Holysz, *J. Amer. Chem. Soc.*, 1953, **75**, 4432.

constants can be estimated. The doublet at lowest field in the spectra of the ketones (20) and (23) can be assigned to the proton (a) next to the nitrogen atom. there is no apparent *meta*-coupling, and $J_{a,b}$ is 10 Hz, The quartet at δ 6·65 p.p.m. in Figure 2a must be assigned to proton (d) and has a major coupling of 13 Hz, with a minor coupling $J_{b,d}$ of 1 Hz. The signal at highest field (overlapping quartets) is due to proton (b) and the last signal (overlapping doublets) to proton (c); from the clearly dirtinguishable major couplings derived from protons (a) and (d) two values for $J_{b,c}$ can be

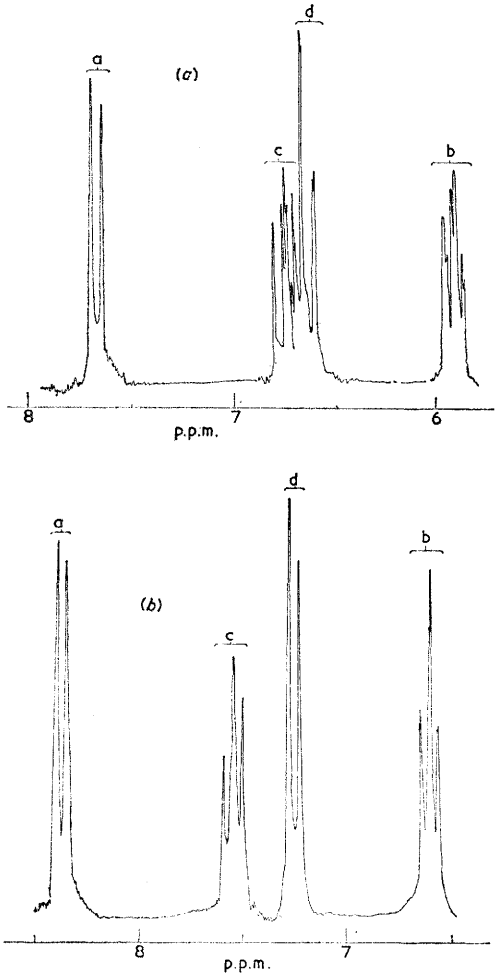



FIGURE 2 (*a*) Pyrroloazepinone (23), in $CDCl_3$; (*b*) pyrroloazepinium salt (24), in TFA

derived which agree well with one another and give a figure of 8 Hz. These values are similar to those of benzo[2,3]tropone, with alternating higher and lower values.[17] In contrast, the n.m.r. spectra of the hydroxyazepinium salts (Figures 1b and 2b) show the expected downfield shift of proton (a); the values of $J_{a,b}$ and $J_{c,d}$ are 10 and 11 Hz respectively and the estimated value for $J_{b,c}$ is now 10—11 Hz ($J_{b,d}$ 1 Hz). The similarity of adjacent coupling constants has been taken as evidence of coplanarity in the seven-membered ring of benzotropylium salts.

Some of this work has appeared in brief communications.[18,19]

## EXPERIMENTAL

All m.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were determined with a Perkin-Elmer 257, n.m.r. spectra with a Perkin-Elmer R10 (60 MHz) (unless otherwise stated), and electronic absorption spectra with a Unicam SP 800 instrument. Chemical shifts are recorded as δ values (p.p.m. from internal tetramethylsilane).

N-(4-*Chlorobutyl*)*pyrrole* (5).—Pyrrole (33·5 g.) was added dropwise at room temperature to a suspension of sodium hydride (24 g., 50% dispersion in oil) in previously dried 1,2-dimethoxyethane (350 ml.) under nitrogen. The mixture was then heated under reflux for 1 hr. The resultant suspension was then blown over with nitrogen into a dropping funnel and added dropwise to a stirred, boiling solution of 4-chlorobutyl toluene-p-sulphonate (135 g.) in 1,2-dimethoxyethane (50 ml.). Boiling was continued for 0·5 hr. and the solution was then stirred for 12 hr. at room temperature. The solvent was evaporated off and the residue taken up in water and extracted with ether. The ethereal extract was dried ($Na_2SO_4$), filtered, and evaporated. Distillation gave the *N*-(4-chlorobutyl)pyrrole (41 g., 50·6%) as a colourless liquid, b.p. 64—66°/0·05 mm. (lit.,[13] 95°/12 mm.).

N-(4-*Cyanobutyl*)*pyrrole* (6).—Prepared (54%) as described by Patterson, Brasch, and Drenko; [13] b.p. 89—90°/0·02 mm. (lit.,[13] 119—120°/3 mm.).

6,7,8,9-*Tetrahydro*-5H-*pyrrolo*[1,2-a]*azepin*-9-*one* (7).—Prepared as described by Patterson, Brasch, and Drenko,[13] except that during the 18 hr. hydrolysis of the intermediate imine, additional portions of aqueous ammonia were added at intervals. Extraction of the aqueous ammoniacal mixture with chloroform, drying of the chloroform solution ($CaCl_2$) and distillation gave the cyclic ketone (7) (49%), b.p. 96—98°/0·05 mm., m.p. 31—32° (lit.,[13] m.p. 32·5—34·5°; yield 31%).

2,3,8,8-*Tetrabromo*-6,7,8,9-*tetrahydro*-5H-*pyrrolo*[1,2-a]-*azepin*-9-*one* (8).—Bromine (6·4 g.) in carbon tetrachloride (10 ml.) was added to a stirred solution of the bicyclic ketone (7) (1·49 g.) in the same solvent (30 ml.) containing calcium carbonate (a few g.). After the addition, stirring was continued for a further 2 hr. and the calcium bromide was filtered off and washed well with carbon tetrachloride. The combined solutions were washed with sodium hydrogen carbonate solution, dried, and evaporated to small volume to give a yellow-brown solid; this gave the *tetrabromoketone* (8) as pale yellow crystals (3·5 g., 75%), m.p. 129—132° (from ether) Found: C, 23·0; H, 1·25; N, 2·8. $C_9H_7Br_4NO$ requires C, 23·2; H, 1·5; N, 3·0%). $\nu_{max.}$ ($CHCl_3$) 1663 $cm.^{-1}$, δ ($CDCl_3$) 7·2 (s, pyrrole H), 6·2—6·5 (2H, m, $N{\cdot}CH_2$), 2·8—3·2 (2H, m, $CH_2{\cdot}CBr_2$), and 2·0—2·5 (2H, m).

6,7,8,9-*Tetrahydro*-5H-*pyrrolo*[1,2-a]*azepin*-9-*ol* (9).—A solution of 6,7,8,9-tetrahydro-5*H*-pyrrolo[1,2-*a*]azepin-9-one (7) (1·49 g.) in absolute ethanol (20 ml.) was treated drop-

[17] D. J. Bertelli, J. T. Gerig, and J. M. Herbelin, *J. Amer. Chem. Soc.*, 1968, **90**, 107.

[18] E. W. Collington and G. Jones, *Tetrahedron Letters*, 1968, 1935.

[19] E. W. Collington and G. Jones, *Chem. Comm.*, 1968, 958.

wise with stirring with a solution of sodium borohydride (0·25 g.) in 2N-sodium hydroxide (0·2 ml.) diluted with water (3 ml.). Stirring was continued at room temperature and the reaction was monitored by the disappearance of the $\lambda_{max.}$ (EtOH) 294 nm. u.v. absorption. After 2·5 hr. the ethanol was removed under reduced pressure and the residue was diluted with water (10 ml.) and extracted with ether (30 ml.). The extract was dried ($MgSO_4$), filtered, and evaporated to leave a pale yellow oil (1·36 g., 90%), which gradually solidified. Crystallisation from light petroleum (b.p. 40—60°) gave the *alcohol* (9) as colourless crystals, m.p. 72—74° (Found: C, 71·6; H, 8·75; N, 9·4. $C_9H_{13}NO$ requires C, 71·5; H, 8·65; N, 9·3%), $\nu_{max.}$ (Nujol) 3260 cm.$^{-1}$ (OH), $\lambda_{max.}$ (95% EtOH) 220 nm. (log ε 3·83), δ ($CCl_4$) 6·4—6·6 (pyrrole α-H), 5·8—6·1 (2H, pyrrole β-position), 4·8—5·1 (1H, m, CH·O), 4·0—4·3 (2H, m, N·$CH_2$), and 1·4—2·4 (6H).

The benzoate (10), prepared in pyridine, was an oil, $\nu_{max.}$ (film) 1715 cm.$^{-1}$, δ ($CDCl_3$) 7·9—8·3 (2H) and 7·2—7·8 (3H) (Bz), 5·9—6·6 (4H, pyrrole ring and C*H*·OBz), 4·0—4·3 (2H, N·$CH_2$), and 1·6—2·4 (6H).

1-(4-*Chlorobutyl*)-3-*methylindole* (12).—The procedure used was as described for compound (5) except that the sodium salt suspension was added to the toluene sulphonate solution at room temperature. From 3-methylindole (9·4 g.), sodium hydride (50% dispersion; 3·4 g.) and 4-chlorobutyl toluene-*p*-sulphonate (18·9 g.) the yield of 1-(4-*chlorobutyl*)-3-*methylindole* (12) was 12·1 g. (76%), b.p. 129—131°/0·25 mm. (Found: C, 70·6; H, 7·35; N, 5·8. $C_{13}H_{16}ClN$ requires C, 70·4; H, 7·3; N, 6·3%), δ ($CCl_4$) 7·0—7·7 (4H), 6·8br (s, indole 2-proton), 4·0 (2H, t, $CH_2$·N), 3·4 (2H, t, $CH_2Cl$), 2·3 (Me), and 1·5—2·1 (4H).

1-(4-*Cyanobutyl*)-3-*methylindole* (13).—Prepared by an adaptation of Smiley and Arnold's method [20] as described for compound (6).[13] From the chloro-compound (12) (10·0 g.) and sodium cyanide (2·21 g.) in dimethyl sulphoxide (25 ml.), 1-(4-*cyanobutyl*)-3-*methylindole* (13), b.p. 148—150°/0·1 mm. was obtained (4·71 g., 49%) (Found: C, 79·0; H, 7·45; N, 13·1. $C_{14}H_{16}N_2$ requires C, 79·1; H, 7·6; N, 13·2%), $\nu_{max.}$ (film) 2235 cm.$^{-1}$, δ ($CDCl_3$) 7·0—7·8 (4H), 6·88 (indole 2-proton), 4·05 (t, $CH_2$·N), 2·35 (Me), 2·2 (t, $CH_2$·CN), and 1·4—2·0 (4H).

The *picrate*, red needles from ether, had m.p. 91—93° (Found: C, 54·3; H, 4·45; N, 15·7. $C_{20}H_{19}N_5O_7$ requires C, 54·4; H, 4·35; N, 15·85%).

*Attempted Cyclisation of the Nitrile* (13).—(*a*) When the procedure described by Patterson, Brasch, and Drenko [13] was used the nitrile (13) was recovered unchanged.

(*b*) A mixture of the nitrile (13) (2·12 g.) and polyphosphoric acid (20 g.) was slowly heated to 110°, when a red-brown colour developed, then to 140°. The mixture was kept at 140° for 1 hr., cooled to 60—70°, and poured on ice–water (500 ml.). The mixture was extracted with ether and the extracts were washed with 5% sodium hydroxide solution, dried, and evaporated to leave a brown oil (0·51 g.). A sample was distilled (bulb tube) to give the *amide* (14), b.p. 200—210°/0·15 mm. $\nu_{max.}$ (film) 3450, 3350, 3195, and 1662 cm.$^{-1}$, δ ($CDCl_3$) 7·0—7·8 (4H), 6·9 (indole 2-proton), 4·08 (t, $CH_2$·N), 2·35 (Me), and 1·3—2·5 (6H). The *picrate*, red needles from ether, had m.p. 78—79° (Found: C, 52·4; H, 5·0; N, 14·95. $C_{20}H_{21}N_5O_8$ requires C, 52·3; H, 4·6; N, 15·25%).

5-(3-*Methylindol*-1-*yl*)*pentanoic Acid* (15).—A solution of the nitrile (13) (2 g.) in ethanol (15 ml.) with aqueous sodium hydroxide (20%; 30 ml.) was boiled for 8 hr. The ethanol was distilled off and the aqueous residue was acidified (2N-HCl) and extracted with ether. The extracts were washed with water, dried ($Na_2SO_4$), and evaporated, leaving an oil which slowly crystallised (2·05 g., 94%). The solid was sufficiently pure to be used in the cyclisation, but a sample was crystallized from light petroleum (b.p. 40—60°) to give the colourless *acid* (15), m.p. 76—77° (Found: C, 72·6; H, 7·3; N, 6·2. $C_{14}H_{17}NO_2$ requires C, 72·7; H, 7·4; N, 6·1%), $\nu_{max.}$ ($CHCl_3$) 1713 cm.$^{-1}$, δ ($CDCl_3$) 10·25 ($CO_2H$), 7·0—7·8 (4H), 6·95 (indole 2-proton), 4·1 (t, N·$CH_2$), 2·35 (Me, overlapping $CH_2$·$CO_2H$), and 1·6—2·1 (4H).

7,8,9,10-*Tetrahydro*-11-*methyl*-6H-*azepino*[1,2-a]*indol*-10-*one* (16).—A mixture of the acid (15) (2·5 g.) and polyphosphoric acid (20 g.) was heated at 95° for 15 min. Working up as described for compound (14), method (*b*), gave, after distillation, a colourless oil (1·15 g., 50%), which slowly crystallized. The *ketone* (16) had m.p. 70—71° [from light petroleum (b.p. 40—60°)] (Found: C, 78·5; H, 6·8; N, 6·6. $C_{14}H_{15}NO$ requires C, 78·5; H, 7·1; N, 6·6%), $\nu_{max.}$ ($CHCl_3$) 1655 cm.$^{-1}$, $\lambda_{max.}$ (95% EtOH) 214, 242, and 313 nm. (log ε 4·16, 4·22, and 4·26), δ ($CCl_4$) 7·8—7·0 (4H, m), 4·28 (t, N·$CH_2$), 2·63 (t, CO·$CH_2$), 2·49 (s, Me), and 1·8—2·2 (m, ·$CH_2$·$CH_2$·).

9,9-*Dibromo*-7,8,9,10-*tetrahydro*-11-*methyl*-6H-*azepino*-[1,2-a]*indol*-10-*one* (19).—Phenyltrimethylammonium tribromide [15] (3·76 g., 0·01 mole) was added to a solution of the cyclic ketone (16) (1·07 g., 0·005 mole) in anhydrous tetrahydrofuran (THF) (15 ml.) at room temperature and the mixture was set aside with occasional shaking for 5 hr. It was then filtered, the insoluble quaternary salt was washed with a little THF, and the combined filtrates were evaporated *in vacuo* to give the *dibromo-ketone* (19) (1·49 g., 80%), which gave yellow prisms, m.p. 118—119° (from methanol) (Found: C, 45·6; H, 3·6; N, 3·8. $C_{14}H_{13}Br_2NO$ requires C, 45·3; H, 3·55; N, 3·8%), $\nu_{max.}$ ($CHCl_3$) 1668 cm.$^{-1}$, δ ($CDCl_3$) 7·2—7·9 (4H) 4·28 (t, $CH_2$·N), 3·0 (t, $CH_2$·$CBr_2$), 2·5 (Me), and 2·0—2·5 (2H).

11-*Methylazepino*[1,2-a]*indol*-10-*one* (20).—A mixture of the dibromo-ketone (19) (4·45 g., 0·012 mole), anhydrous lithium chloride (1·5 g., 0·036 mole) and dry dimethylformamide (DMF) (300 ml.) was boiled and stirred under nitrogen for 1·5 hr. The mixture was cooled, and the DMF was removed under reduced pressure. Water was added, and the aqueous solution was extracted with ether. The extracts were dried ($Na_2SO_4$), and evaporated, to leave the *azepinoindolone* (20) (2·1 g., 83%) as an orange solid, m.p. 124—125° (from methanol) (Found: C, 80·1; H, 5·15; N, 6·8. $C_{14}H_{11}NO$ requires C, 80·35; H, 5·3; N, 6·7%), $\nu_{max.}$ ($CHCl_3$) 1656, 1603, and 1570 cm.$^{-1}$, $\lambda_{max.}$ (95% EtOH) 208, 226, 292, and 329 nm. (log ε 4·14, 4·28, 4·55, and 3·99), $\lambda_{max.}$ (100% $H_2SO_4$) 233, 272, 327sh, 336, 550sh, and 611 nm. [log ε 4·04, 4·06, (—), 4·64, (—), 3·04];* n.m.r. in Figure 1.

10-*Hydroxy*-11-*methylazepino*[1,2-a]*indolium Bromide* (21).—Treatment of a solution of compound (20) (0·6 g.) in chloroform with dry hydrogen bromide gave almost black crystals of the *bromide* (quantitative), m.p. >115° (decomp.) (Found: C, 57·5; H, 4·0; N, 4·7. $C_{14}H_{12}BrNO$ requires C, 57·9; H, 4·15; N, 4·8%).

1,2,3,8,8-*Pentabromo*-6,7,8,9-*tetrahydro*-5H-*pyrrolo*[1,2-a]-*azepin*-9-*one* (22).—A solution of bromine (8·0 g.) in carbon

* These figures were incorrectly quoted in ref. 18.

[20] R. A. Smiley and C. Arnold, *J. Org. Chem.*, 1960, **25**, 257.

tetrachloride (40 ml.) was added slowly at room temperature to a stirred solution of the cyclic ketone (7) (1·49 g.) in carbon tetrachloride (10 ml.) with suspended calcium carbonate (*ca.* 3 g.). The stirring was continued for 5 hr. after the addition of bromine. Work-up as described for compound (8) gave a yellow solid (5·07 g., 93%) which gave the *pentabromo-ketone* (22), m.p. 151—155° (from methanol) (Found: C, 19·5; H, 1·1; N, 2·6. $C_9H_6Br_5NO$ requires C, 19·9; H, 1·1; N, 2·6%), $\nu_{max.}$ ($CHCl_3$) 1680 cm.$^{-1}$, δ ($CDCl_3$) 4·37 (t, $CH_2$·N), 3·0 (t, $CH_2$·$CBr_2$), 2·0—2·4 (2H, m).

1,2,3-*Tribromopyrrolo*[1,2-a]*azepin*-9-*one* (23).—The procedure was as described for compound (20). From the pentabromo-ketone (22) (5·44 g., 0·01 mole), lithium chloride (1·27 g., 0·03 mole) and dry DMF (200 ml.) the *pyrrolo-azepinone* (23) (3·02 g., 79%) was obtained, as yellow needles, m.p. 187—189° (from methanol) (Found: C, 27·9; H, 1·03; N, 3·8. $C_9H_4Br_3NO$ requires C, 28·3; H, 1·05; N, 3·6%), $\nu_{max.}$ ($CHCl_3$) 1662 and 1612 cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 208, 244sh, 252sh, and 279 nm. [log ε 4·05, (—), (—), and 4·40], $\lambda_{max.}$ (100% $H_2SO_4$) 239, 269, 297, 378, and 477 nm. (log ε 4·22, 4·27, 4·59, 3·87, and 3·2); n.m.r. spectra in Figure 2.

1,2,3-*Tribromo*-9-*hydroxypyrrolo*[1,2-a]*azepinium Bromide* (24).—Treatment of a solution of pure azepinone (23) in chloroform with dry hydrogen bromide gave reddish-orange crystals of the *azepinium bromide* (24), m.p. >125° (decomp.) (Found: C, 23·0; H, 1·0; N, 3·0. $C_9H_5Br_4NO$ requires C, 23·3; H, 1·1; N, 3·0%).

1,2,3-*Tribromo*-9-*ethoxypyrrolo*[1,2-a]*azepinium Fluoroborate* (25).—A solution of the azepinone (23) with excess of triethyloxonium fluoroborate in methylene chloride was boiled (0·5 hr.) and cooled to give red crystals of the *ethoxyazepinium fluoroborate* (25) m.p. >155° (decomp.) (Found: N, 2·85. $C_4H_9BBr_3F_4NO$ requires N, 2·8%), $\nu_{max.}$ (KBr) 1120—1020 cm.$^{-1}$.

*Reduction of Pyrroloazepinone* (23).—A solution of the azepinone (23) (0·76 g.) in 95% ethanol (300 ml.) was hydrogenated to completion at atmospheric temperature and pressure over 10% palladium–charcoal (0·25 g.) (uptake was 5 mol.). The filtered solution was evaporated, to leave a brown gum. Water was added, and the mixture was extracted with ether. The dried extracts were evaporated to leave an almost colourless oil (0·14 g.), which solidified to a white solid, identical in m.p. and n.m.r. spectrum with the ketone (7).

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